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PSP RESINS, NEW MATRICES WHICH CAN BE HARDENED BY
THERMAL TREATMENT FOR USE IN COMPOSITE MATERIALS
RESISTANT TO HEAT AND FIRE

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FIGURES

PSP RESINS, NEW MATRICES WHICH CAN BE HARDENED BY
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RESISTANT TO HEAT AND FIRE

M. Ropars, B. Bloch and B. Malassine¹

I. Introduction

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In aeronautics and space technology, ways are being sought to replace the conventional metallic substances currently used in the construction of certain vehicular structural elements with reinforced plastics. This alternative offers several advantages, but the fundamental attraction is most often the excellent performance/density ratio of these new substances.

Nevertheless, wider use of these products still depends on the ability of currently available commercial resins to embody a variety of characteristics which will enable them to meet the needs of the aeronautics and space sector. Such substances must have excellent mechanical properties, and must retain these properties regardless of environmental stress (e.g., humidity, in particular), and in spite of the high temperatures encountered during supersonic flight. Such substances should also meet the obvious fire resistance requirements. Determining factors include inflammability, the density and toxicity of gases released during combustion, and mechanical resistance to burning for a limited period of time. Furthermore, since industrial development of various high-performance polymers will be pursued primarily for economic reasons, the proposed resins should be such

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*Numbers in the margin indicate pagination in the foreign text.

that they can be prepared from simple and relatively inexpensive 2
compounds using nonrestrictive technologies.

PSP resin (Ropars and Bloch French Patent No. 2,261,296 - 1974 and U.S. Patent No. 3,994,862 - 1976), which is the subject of this report, appears to have qualities and properties which meet the above-mentioned requirements. The resin was discovered and studied at the ONERA Organic Synthesis and Composite Materials Laboratory. Development work at the SNPE Bouchet Research Center in collaboration with ONERA and with the assistance of the IRCHA Materials Laboratory has made the synthesis and experimental use of this resin possible at the industrial level.

II. Prepolymer and Pure Resin

PSP prepolymers are thermosetting oligomer mixtures obtained by polycondensation of aromatic aldehydes with methylated pyridine derivatives (Figure 1). Strong attraction between heterocycles, double bonds and benzene rings tend to favor thermostability and resistance to fire.

Polycondensation can be interrupted at various points during synthesis, thus engendering a variety of products with different viscosities. These products range from impregnation solutions to injection resins and powders which can be molded.

These prepolymers are entirely soluble in the polar aprotic solvents such as DMF, DMAc and NMP (or, under certain conditions, in alcohols and keto-alcoholic mixtures), on which are based the 6032 and 6022 PSP resins developed by SNPE for industrial impregnates.

Since polymerization takes place only above 150°C, the preparation and consequently the preimpregnates derived therefrom are

extremely stable at ambient temperature; the latter are also impervious to humidity, even under highly hygrometric conditions.

Figure 2 shows the physical properties of the pure resin after the powder has been heated and pressure-molded. The curves in Figure 3 indicate that the thermal breakdown of this substance begins at 300°C, and increases rapidly as the temperature approaches 450°C. In an inert atmosphere, the pure resin yields a 65% pyrolytic residue at approximately 1000°C.

III. Production of Laminates

/3

A. Impregnation

The use of raw synthesized resin as an impregnation liquid for PSP 6030 was abandoned due to the methyl-pyridine odor emitted during pressure-molding. Furthermore, utilization of resinous solutions with aprotic solvent bases was discontinued, since such solutions inhibit the extensive procedures at high temperatures which are required in order to eliminate all traces of solvents whose presence would cause porosity of the compounds and a consequent degradation of the latter's thermal and mechanical properties. Finally, since the solubility of alcohols in the resin is limited, industrial impregnates cannot be prepared at ambient temperature with such solvent-based resins.

One notable characteristic of the 6032 and 6022 impregnation resins is that in solution, their viscosity can be varied in a non-toxic keto-alcoholic mixture with a low boiling point, which can easily be removed at about 200°C. Preferred viscosity values are from 200 to 500 cp. Industrial impregnates have been prepared by SNPE in continuous carbon-core strips 34 cm wide, and by Genin in fiberglass strips 1.2 m wide. The preimpregnate thus obtained is flexible, has a low volatile material quotient and can be stored for several months at ambient temperature.

B. Preparation of Preimpregnates

Pressure molding of preimpregnates can be carried out in 3 hours at 200°C. Pressure on the order of 5 kg/cm² is applied after the first hour, but is reduced as the gel point is neared. While pressure is being applied, the countermold is held away from the prepreg in order to avoid any creepage at this stage.

Autoclave pressure molding is also carried out in two steps. A vacuum is obtained both inside and outside the bag during the first hour. Subsequently, the vacuum outside the bag is replaced by air pressure of 5 kg/cm² for a period of 2 hours.

It has been found that the introduction of thixotropic agents into the prepolymer in order to modify the flow rate has no effect on the mechanical properties of the laminate.

Subsequent to either molding method, the geometrical stability of the laminate above 110 to 120°C and its maximum thermostability are obtained by means of non-pressurized treatment at 225 to 250°C. These post-treatments are carried out on the mold in order to avoid flow deformation of the pieces.

C. Other Preparation Methods

Experimental forming attempts by means of injections of suitably condensed prepolymers and by filament spinning have been most encouraging, and these techniques should become viable in the near future.

IV. Properties of Laminates

A. Initial Mechanical and Thermal Properties

The thermomechanical properties of PSP laminates were estimated by measurement at various temperatures of the laminates'

resistance to flexure rupture and interlaminary shear, and of their flexure modulus according to ASTM standards D790-66 and D2344-72. Test pieces were cut from planar sheets 2.5 and 3 mm thick with volumetric fiber contents on the order of 55 to 60% and with nil porosity or porosity less than 3%.

With regard to carbon-reinforced laminates, Figure 4 illustrates the importance of preceding the 250°C post-treatment (which is essential in order for the substance to have adequate resistance at high temperatures) by a short period at 225°C in order to preserve the quality of flexure rupture resistance at ambient temperature.

Figure 5 summarizes the results of mechanical tests carried out at ambient temperature and at 250 or 200°C with various types of reinforcement. The values obtained agree well with the resistances of the reinforcing agents themselves except in the case of Kevlar 49, which did not stand up to treatments at or above 200°C and for which compression entailed a degree of defibrination. /4

B. Resistance to Thermal Aging

The curves in Figure 6 illustrate the evolution of flexure rupture resistance of Courtaulds HTS Grafil unidirectional PSP carbon laminates as a function of the length of time the test pieces were subjected to various temperatures. The values shown were taken at the temperatures at which aging occurred.

The value of 1250 MPa obtained at 200°C remained constant for 10,000 hours (the duration of testing). A decrease on the order of 10% was observed after 300 hours at 250°C, and this value was likewise hardly affected after 100 hours at 300°C. As illustrated in Figure 7, the maintenance of flexure rupture resistance between 350 and 400°C is such that missile applications can be envisioned.

Figure 8 shows the evolution of interlaminary shear rupture resistance during aging at 250°C. /5

The result shown in Figure 9 were obtained for laminates with AS carbon fiber reinforcement.

The thermal resistance of type 1581 A-1100 fiberglass-reinforced PSP laminates in continuous use appears to be somewhat less. However, results indicated that flexure and shear rupture resistance values obtained from tests equivalent to 1000 hours at 150°C should remain satisfactory for longer periods, and probably also at slightly higher temperatures.

C. Resistance to Humidity

The effect of humidity on the mechanical and thermal properties of HTS industrial carbon-fiber PSP laminates was ascertained by a series of tests involving immersing unprotected samples in boiling water. The absorption of water observed was very slight, and occurred almost entirely during the first few hours of testing. The quantity of water absorbed did not exceed 0.7% of the mass of the laminate. Similarly, in spite of the rigorousness of this test, no drop in flexure rupture resistance was noted, either at ambient temperature or at 250°C. Shear resistance was also very stable at ambient temperature, while a decrease of not more than 20%, dating from the beginning of immersion, was noted at 250°C (Figure 10).

A more conventional test was carried out on T300 carbon-reinforced laminates. Pre-cut test pieces were subjected to aging for 700 hours at 70°C and 95% relative humidity. Resistance to shear of 97 MPa at ambient temperature was obtained for test pieces with an initial value of 108 MPa. /6

Analogous tests are currently being carried out on type 1581 A-1100 fiberglass-reinforced PSP laminates.

D. Resistance to Mechanical and Thermal Fatigue

During three-point wave flexure testing at ambient temperature, HTS unidirectional carbon PSP-6030 laminates remained unaffected by 3×10^7 cycles at a frequency of 25 Hz under maximum stress equivalent to 70% of the rupture value. During alternating symmetrical flexure tests with one end of the sample piece fixed in place, stress of ± 650 MPa was applied at a frequency of 25 Hz for 4×10^7 cycles, the extreme flexure moment decreased no more than 5%.

An initial estimate of the resistance to thermal fatigue was made by means of tests at 1500 to 2000 cycles from ambient temperature to 225°C, with 5-minute stages at each temperature. These tests apparently caused no decrease in mechanical and thermal properties.

E. Resistance to Chemical Agents

With respect to mechanical properties, immersion testing of 6030-Courtaulds HTS unidirectional laminates in acidic and basic mediums for 7 days at ambient temperature in accordance with ASTM standard D543-43 illustrated the complete imperviousness to chemical agents of these laminates. Figure 11 also illustrates the only slight weight gain as well as good resistance of the laminates to alkaline agents, which is usually the weak point of polyimide resins.

F. Fire Resistance

In order to make comparisons with current industrial resins, the PSP resins whose fire behavior was studied were in the form of laminates.

The limit oxygen value, which measures the minimum oxygen content necessary to sustain combustion with flame, was determined

according to AFNOR standard T51-071 (comparable to ASTM standard D2863-70) for test pieces 2.5 mm thick. The AS T300 unidirectional carbon-reinforced PSP laminates had a limit oxygen value of 60% $\pm 1\%$. The limit oxygen value of laminates with fiberglass reinforcements was found to be 90% $\pm 1\%$.

Other tests utilizing the most widely known current techniques for determining the fire resistance of organic compounds intended for aeronautic construction were carried out by the Toulouse Aeronautics Testing Center. Fiberglass-reinforced PSP resins were studied with respect to both self-extinguishability and toxic gas or smoke emission. Inflammability tests were carried out on vertical elements with lighting times of 60 seconds and 12 seconds, corresponding respectively to tests on structural hatchways (class "a") and cabin walls (class "b"). Emission toxicity tests were carried out with and without flame in an NBS chamber equipped with Draeger detection tubes.

The results obtained are summarized in Figures 12, 13 and 14, /7 which include comparisons with other fiberglass-reinforced resins.

The results appear to indicate that the behavior of PSP laminates is significantly better than that of polyimides, and is almost equivalent to that of phenolic resins, whose mechanical and thermal properties are distinctly inferior. /8

It should be noted that self-extinction is virtually instantaneous, and is very rapid for thin layers subjected to prolonged lighting. The length of the substance burned is either nil or very short, and the emission of fumes is slow. The fumes emitted are not dense, and have a low carbon monoxide content. For a nitrogenous resin, the quantity of hydrocyanic acid and nitrous gases released is remarkably small. The pyrolysis gas value of 50, estimated by a NASA test at 119 to 130, confirms the value of this substance.

Possible utilization for thermal protection was studied in plasma stream and/or oxyacetylene torch tests. Results indicate that between 1800 and 3000°C, the test pieces retain their cohesion and preserve a portion of their mechanical properties.

V. Conclusion

As matrices for composites, PSP thermosetting resins combine a variety of worthwhile properties, especially with respect to the aeronautics and space industry. Their thermostability, fire resistance and resistance to humidity may enable these resins to fill a currently vacant position in the field.

Economic forecasts appear to indicate excellent competitive potential for this type of product. The prepolymer can be prepared easily from simple compounds; it can be obtained in varying degrees of viscosity, thus permitting utilization of different forming techniques; it can be prepared at low pressure, and volatile components can be easily removed. Due to these properties, the resins appear to be immediately practicable raw materials, not only for high-temperature applications but also for use in conjunction with substances utilized at or near ambient temperature.

The resins are prepared at the pilot level by SNPE, and industrial carbon-fiber and fiberglass impregnates have already been realized.

FIGURES

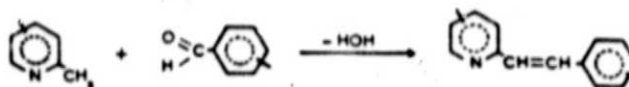


Fig. 1. Chemistry of PSP resins.

(1)	masse volumique	1,14
(2)	coefficient de dilatation linéaire	$6.10^{-5}/^{\circ}\text{C}$
(3)	résistance à la rupture en flexion à l'ambiante	100 MPa
(4)	module de flexion	2500 MPa

Fig. 2. Properties of the pure resin.

KEY:

- (1) Volumetric mass
- (2) Linear expansion coefficient
- (3) Flexure rupture resistance at ambient temperature
- (4) Flexure modulus

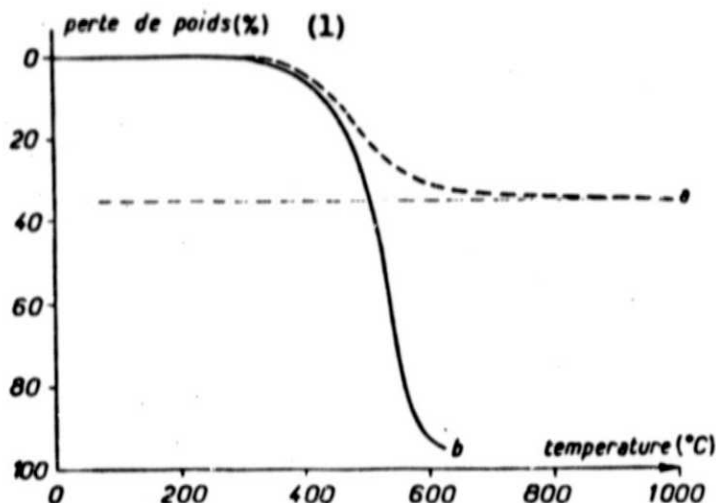


Fig. 3. Thermogravimetric analysis of PSP resins in argon (a) and in air (b) after post-treatment.

KEY:

(1) Weight loss in percent

Résistance à la rupture (MPa) (1)		(2) Sans post-traitement	(3) après 16h à 250°C	(4) après 2h/225°C + 8h/250°C
en flexion (5)	à l'ambiante (6)	1800	1250	1700
	à 250°C (7)	≈ 400	1300	1300
en cisaillement (8)	à l'ambiante (6)	90	90	90
	à 250°C (7)	≈ 30	70	70

Fig. 4. Effects of post-treatments on thermomechanical properties of Courtaulds HTS 6032 uni-directional carbon laminates.

KEY:

- (1) Rupture resistance (MPa)
- (2) Without post-treatment
- (3) After 16 hours at 250°C
- (4) After 2 hours at 225°C and 8 hours at 250°C
- (5) Flexure
- (6) At ambient temperature
- (7) At 250°C
- (8) Shear

(3) Propriétés mécaniques		Tempé- rature	(1) Renforts unidirectionnels						Tissus style 1581(2)	
			CARBON			BORE (4)	Kevlar 49	VERRE E (A1100) (b)		VERRE E (TF 910) (c)
			AS	MTS	IMS					
(8) Flexion	Resistance	20°C	1 400	1 700	1 100	1 800	600	1 000	540	540 à 580
		250°C	1 000	1 250	—	1 480	1 900	1 000*	530*	(9)
Module (10)		20°C	90,000	110,000	150,000	134,750	80,000	40,000	30,000	29,000
		250°C	90,000	110,000	—	121,700	—	40,000*	30,000*	—
Cisaillement (11) Interlaminaire (12)		20°C	100	90	50	90	40	50	48	50 à 54
		250°C	70	70	40*	62	—	40*	31*	(13) JDR

* Mesuré à 200°C

(a) Avec résine 6032 - Imprégnation SNPE (T300-6000 f11)

(b) Avec résine 6032 - Imprégnation IRCMA

(c) Avec résine 6022 - Imprégnation Genin - Cycle 4h à 200°C + 2h à 225°C sous 10bars)

(14)

Fig. 5. Mechanical properties (in MPa) of laminates with a PSP matrix (6030, 6032, 6022) at 20°C and 250°C.

KEY:

- (1) Unidirectional reinforcements
(2) Type 1581 substances
(3) Mechanical properties
(4) Boron
(5) Glass "E" (A-1100)
(6) Glass "E" (A-1100) (b)
(7) Glass "E" (TF-910) (c)
- (8) Flexure
(9) 540 to 580
(10) Modulus
(11) Shear
(12) Interlaminary
(13) 50 to 54
(14) *Measure. at 200°C

- (a) With 6032 resin - SNPE impregnation (T-300/6,000 strand)
(b) With 6032 resin - IRCMA impregnation
(c) With 6022 resin - Genin impregnation: cycle of 4 hours at 200°C and 2 hours at 10 bars

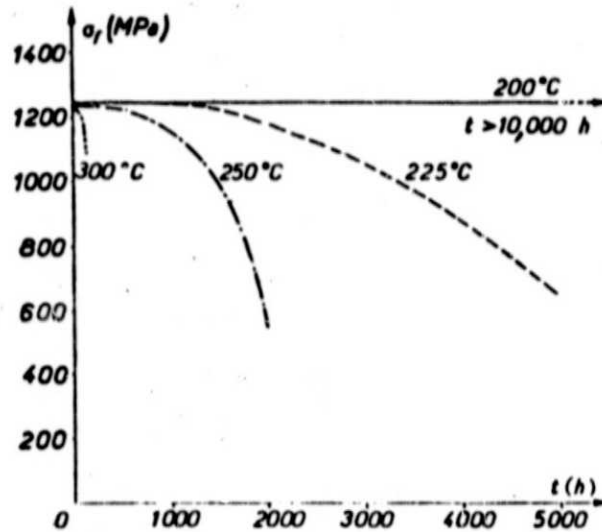


Fig. 6. Evolution of flexure rupture resistance of 6030-Courtaulds HTS unidirectional laminates as a function of the duration of thermal aging

$$55 \% \leq \tau_{f_{vol}} \leq 60 \% \quad 0 \leq \tau_{dc} \leq 3 \%$$

Measured at the aging temperature.

Temperature	Résistance à la rupture en flexion (MPa)	
	Après 20 mn (2)	Retention
350°C	1000	850 après 24h (3)
400°C	950	900 après 8h (4) 450 après 16h (5)
450°C	200	--

Fig. 7. Thermomechanical limits of 6030-Courtaulds HTS unidirectional laminates.

KEY:

- (1) Flexure rupture resistance (in MPa)
- (2) After 20 minutes
- (3) 850 after 24 hours
- (4) 900 after 8 hours
- (5) 450 after 16 hours

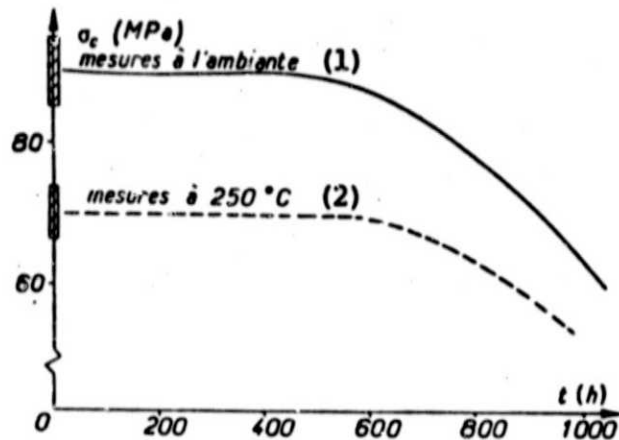


Fig. 8. Evolution of shear rupture resistance of 6030-Courtaulds HTS unidirectional laminates as a function of the duration of aging at 250°C.

KEY:

- (1) Measured at ambient temperature
- (2) Measured at 250°C

Temps de vieillissement à 250°C (1)		0	500 h	1000 h	1500 h	2000 h
Perte de poids en % (2)		0	1%	2.5%	3.5%	3.5%
(3)	Résistance en flexion (MPa)	20°C	1550	935	955	923
		200°C	1300	886	864	848
(4)	Module de flexion (MPa)	20°C	106200	108750	98780	95750
		200°C	94660	104250	96410	91960
(5)	Cisaillement (MPa)	20°C	103	66,5	64	52
		200°C	74,5	67	58,6	58,8

Fig. 9. Aging at 250°C of AS/6030 unidirectional carbon laminates.

KEY:

- (1) Aging time at 250°C
- (2) Weight loss in percent
- (3) Flexure resistance (MPa)
- (4) Flexure modulus (MPa)
- (5) Shear (MPa)

Durée d'immersion dans l'eau bouillante (1)			0	100h	350h	750h	1000h
(2) Résistance à la rupture (MPa)	(3) en flexion	à l'ambiante (4)	1650	1700	1650	1600	1650
		à 250°C (5)	1200	1200	1200	—	1250
	(6) en cisaillement	à l'ambiante (4)	90	90	95	86	88
		à 250°C (5)	70	55	—	55	55
(7) Absorption d'eau			0	0.7%	0.7%	0.7%	0.7%

Fig. 10. Accelerated humid aging of 6030-Courtaulds HTS unidirectional laminates.

KEY:

- | | |
|-------------------------------------|----------------------------|
| (1) Immersion time in boiling water | (4) At ambient temperature |
| (2) Rupture resistance (MPa) | (5) At 250°C |
| (3) Flexure | (6) Shear |
| | (7) Water absorption |

Agent chimique (concentration) (1)	Prise de poids (%) (2)
HCl 10 %	1.4
HNO ₃ 10 %	1.0
H ₂ SO ₄ 30 %	0.9
NH ₄ OH 10 %	0.4
NaOH 10 %	0.2
Atmosphère ambiante (3)	0.2

Fig. 11. Resistance of 6030-Courtaulds HTS laminates to chemical attack after immersion for 7 days at ambient temperature.

KEY:

- | |
|--------------------------------------|
| (1) Chemical agent and concentration |
| (2) Water intake in percent |
| (3) Ambient atmosphere |

RESIN		(1) Nombre de plis	DUREE D'EXTINCTION (sec) (2)		LONGUEUR BRULEE (cm) (3)	
			class a	class b	class a	class b
PSP	6030	4	0	7	1.7	0.4
		12	0	0	1.4	0
		21	0	0	0	0
	6032	3	0	1	2.4	1
POLYIMIDE		4	4	28	5.5	2.8
PHENOLIQUE 1 (4)		3	0	1	4.2	3.5

Fig. 12. Inflammability tests on type 1581 fiberglass-reinforced laminates according to FAR-2532-25853 standard for classes (a) and (b).
(Lighting times: 60 seconds and 12 seconds.)

KEY:

- | | |
|--------------------------------|--------------------------|
| (1) Number of plies | (3) Length burned in cm. |
| (2) Extinction time in seconds | (4) Phenolic 1 |

RESIN		Poids de l'échantillon (g) (1)	CONCENTRATION (ppm)							
			CO ₂		CO		HCN		NO + NO ₂	
			SF	AF	SF	AF	SF	AF	SF	AF
PSP	6030	34.2	800	9000	30	200	1	6	0.5	10
	6032	6.5	1500	15000	42	200	trace	3	0	7
POLYIMIDE		10.5	--	--	100	500	1	30	4	50
PHENOLIQUE 2 (2)		7.5	--	--	100	200	0	0	0	0

Fig. 14. Toxicity of combustion gases of type 1581 fiberglass-reinforced laminates measured in an Aminco NBS chamber, with flame (AF) and without flame (SF).

KEY:

- | | |
|----------------------------|----------------|
| (1) Weight of sample in g. | (2) Phenolic 2 |
|----------------------------|----------------|

RESIN	Nombre de plis (1)	Poids de l'échantillon (g) (2)	DENSITE OPTIQUE SPECIFIQUE (3)						DENSITE OPTIQUE SPECIFIQUE MAXIMALE (7)		
			(4)		(5)		(6)		SF	AF	
			après 1 mn	après 3 mn	après 5 mn	après 3 mn	après 5 mn	après 5 mn			
6030	14	34.2	0	0	0	0	0	1	1.7	3.3 (8) après 30 mn	33 (9) après 27 mn
	PSP 6032	6.5	0	0	0	0	1	1	1	2 (10) après 20 mn	4 (11) après 13 mn
POLYIMIDE	4	10.5	0	4.5	0	18	2.3	32	15 (12) après 22 mn	46 (13) après 11 mn	0
PHENOLIQUE 1 (14)	3	2.7	0	0	0	0	0	0	0	0	0
PHENOLIQUE 2 (15)	3	7.5	0	0	0	0	0	1	0	non atteinte après 20 mn (16)	non atteinte après 20 mn (16)

Fig. 13. Emission of fumes by type 1581 fiberglass-reinforced laminates in an Aminco NBS chamber, with flame (AF) and without flame (SF).

KEY:

- (1) Number of plies
- (2) Weight of sample in g.
- (3) Specific optical density
- (4) After 1 minute
- (5) After 3 minutes
- (6) After 5 minutes
- (7) Maximum specific optical density
- (8) After 30 minutes
- (9) After 27 minutes
- (10) After 20 minutes
- (11) After 13 minutes
- (12) After 22 minutes
- (13) After 11 minutes
- (14) Phenolic 1
- (15) Phenolic 2
- (16) Not attained after 20 minutes